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(54) Compositions useful in improving dough and bread, and their use

(57) Compositions consisting essentially of calcium peroxide, iron salt(s) and ascorbic acid which provide improver activity suitable for the replacement of known bromate improvers in bread dough by providing for reproducible, controllable conversion of ascorbic acid to dehydroascorbic acid. Also processes for their use.

GB 2 264 429 A

COMPOSITIONS USEFUL IN IMPROVING DOUGH AND BREAD, AND THEIR USE

This invention relates to compositions for improving bread and dough, methods of making dough and methods of making bread.

Commercial baking of bread conventionally uses oxidants ("improvers") at low levels to optimise the complex balance of dough properties which leads to high quality bread.

For many years bromate salts of calcium, sodium and potassium (particularly potassium) have been the oxidative improvers of choice because of their relatively slow action, their tolerance to mixing and their presumed safety at normal use levels.

Recent animal studies have however suggested a link between bromates and cancer in animals. In California, Proposition 65 has proposed investigation of bromates as a possible health hazard.

The amount of oxidant required by the baker depends on the particular bread-making process employed. The most common method, the so called "sponge and dough method", conventionally requires only about 15 to 20 parts per million by weight (ppm) of potassium bromate in the dough. Other doughs require up to 75ppm potassium bromate (the current maximum amount permitted by law) and sometimes even this amount must be supplemented by other

improvers.

A variety of other improvers is known. Among the known improvers are L-ascorbic acid (hereinafter ascorbic acid - "AA") and azodicarbonamide ("ADA"), the latter being known as a rapid-acting improver for certain special purposes.

Neither AA or ADA is able, even at its maximum legally-permitted level, to meet the ideal oxidation requirements of certain types of baking e.g. those known as "No Time", "Frozen Doughs", "Cuban" and others.

It would be desirable to provide new improver systems for dough and bread making, and in particular systems which could reduce or eliminate the need to use bromate.

According to the present invention, a composition suitable for use as an improver for dough for bread making comprises calcium peroxide, ascorbic acid and a food-acceptable iron salt such as ferrous sulphate.

We find that such a composition provides a way of obtaining an unexpectedly good improving action from AA. Furthermore, the composition may be provided as a dry, storage stable composition e.g. a powder, which is therefore practical to store and use.

Chemistry within dough is subtle and it is difficult to explain with certainty why the present composition is so effective. Nevertheless, the following observations may be relevant.

AA is a reducing agent. It is believed that the (known) improving action of AA in baking is actually due to an oxidised form, dehydro-L-ascorbic acid (DHA). DHA is thought to be formed from AA during breadmaking, particularly in the dough mixing process, by reaction with entrained oxygen (from entrained air), that reaction being catalysed by an enzyme, ascorbic acid oxidase, which is naturally present in flour.

This belief is supported by the known fact that the effectiveness of AA as an improver varies when different kinds of flour are used e.g. from different locations, different types of environment, different pre-mixing storage or different treatment history. These various flours may have varying quantities of enzymes. The effectiveness of AA also varies according to the dough mixing methods used, and it is known that certain mixing methods (such as "continuous", "Tweedy" and others) have low air entrainment.

We believe that the present invention may be providing an alternative mode whereby AA can be oxidised to the active improver species DHA. This mode, being artificially introduced, can be independent of potentially variable natural concentrations of enzymes and content of entrained air. The present composition can also be made using materials which are acceptable for food use. It is believed that, under the conditions of use, calcium peroxide is a source of hydrogen peroxide

which oxidises the AA under the catalytic activity of the iron salt. The oxidation may be taking place on or just before addition into the flour mixing process.

Optional features of the invention include the following.

The composition may comprise additionally a food-acceptable bulking agent.

The composition may contain azodicarbonamide, and the azodicarbonamide may if wished be encapsulated with a food-acceptable encapsulating agent.

The composition may contain a food-acceptable acid. This may be needed for adjustment of the system to a pH suitable for the desired reaction. Preferred acids are solid at ambient temperatures, for convenient incorporation in a dry composition.

The composition may contain benzoyl peroxide. Such compositions have been found to show an increased improver effect.

The compositions may be essentially inert solids whose ingredients are substantially non-reactive with one another until the compositions are dispersed, e.g. dissolved, in water. In aqueous solution, reactivity is normally enhanced at pH values below 7.

We find that improver properties comparable to those previously obtained with bromate salts can be achieved, if these compositions are used e.g. in aqueous solution at pH below 7.

In another aspect, the invention provides a method of making dough in which calcium peroxide, ascorbic acid and an iron salt are incorporated into the dough.

In a further aspect, the invention provides a method of making bread in which dough is made as stated above.

We note that in the prior bread-making art, US-A-3954999 describes the use of certain hydrated salts to reduce explosion hazards in doughs containing an oxidising agent selected from a list including potassium bromate and calcium peroxide, a flour maturing agent such as azodicarbonamide, and optionally other additives selected from a list including ascorbic acid. One in the long list of suggested hydrated salts is ferric chloride hexahydrate. However there is no specific disclosure of the use of any of calcium peroxide, ascorbic acid and ferric chloride hexahydrate, still less any suggestion of the advantageous effects now found by us.

DETAILED DESCRIPTION

Compositions embodying the invention may be prepared by simple mixing or blending of the ingredients. All three components (calcium peroxide, AA and iron salt) need to

be present simultaneously in the composition and are crucial to the transformation. The absence of any one of the components will affect the transformation seriously.

Blending of the ingredients into a dry powdery composition may be accomplished by mixing methods well known in the art.

The composition may also be created directly in a dough by adding the ingredients separately directly to a dough and adjusting the pH of the dough to the desired range.

Once blended into a dry powdery composition, the composition may be blended directly into a dough employing standard methods known in the art for blending ingredients into dough.

Once blended into the dough, standard treatment procedures known to one of skill in the art for dough mixing, dough development and baking applicable to the type of dough may be applied to manufacture the finished bread. Bread can be prepared, using embodiments of the composition aspects of the invention, with properties including higher specific volume and finer crumb than bread prepared from doughs otherwise containing identical ingredients but lacking the combination of the peroxy compound, the AA and the iron salt. In addition, the properties including specific

volume and crumb size, of bread prepared from doughs using the presently-disclosed techniques, may approximate those of breads prepared from comparable doughs improved with bromate.

The ingredients of the invention may be added to the dough at any time during its preparation or development but it is preferred for maximum effect that addition take place during the dough mixing stage.

Instead of blending the substances of the invention directly into the dough, they may be predissolved in water or flour brews (slurries) and then blended into the dough mixture.

If the composition does not already contain sufficient food approved acid to reduce the pH of the water solution of the composition whether it be in the water solution premix, in solution in a flour brew or in solution in the water in the dough, the pH is preferably adjusted at the time of initial dissolution of the composition.

The aqueous medium (either as a premix or in the dough itself) in which the composition is dissolved should preferably have a pH below 7, preferably from about 2.0 to about 5.50 and more preferably from about 3.60 to about 4.20.

If the composition does not already contain

sufficient food approved acid to provide the desired pH, sufficient food approved acid may be added while monitoring the pH during addition with conventional pH measuring equipment. A solid food approved acid such as citric acid or $Ca(H_2PO_4)_2$ may be included as one of the ingredients of the composition.

Since normal dough pH values range from about 5.5 to 6.0 and can run as low as 4.0, depending on the baking method, the quantity of acid required to be included to provide an aqueous solution in the desired pH range, when solution directly in the dough is intended, may vary widely or acid addition may even be unnecessary.

Where solution in water prior to addition to the dough is intended, since there will be no natural buffer action from any of the other ingredients which might normally be present in such a procedure, the presence of acid in solution to provide the desired pH range will normally be required. If solution in a flour brew is intended, flour provides a natural buffer in the range from about pH 4.0 to about 6.0, the presence of additional acid in any solution will be a convenience to assure a consistent pH environment for the transformation of AA to DHA. In any event, if insufficient acid is supplied in solution by the composition, additional acid

to adjust the pH to a desired range may always be added by the user employing any of the acidic materials normally employed by bakers to acidify dough.

Approximately 1.0 part by weight AA to about 0.75 part by weight calcium peroxide is a convenient ratio although this ratio may vary somewhat. A ratio of about 1.0 part by weight AA to at least about 0.3 part by weight iron salt is apparently necessary, but these proportions may vary from this ratio to provide increasing proportions of iron salt. The rate of transformation of AA to DHA has been found to be dependent on the concentration of the iron salt. A typical composition will have AA to calcium peroxide to iron salt in the ratio of 1.0 to 0.75 to 0.3 all in parts by weight. These are based on anhydrous Ca peroxide.

The amount of the composition employed to provide the improving effective amount of the composition in the dough may also vary widely depending on the effect desired. One of skill in the art will also recognize that the rate of addition will also have influence on the improver effect. One of skill in the art will be able to control the desired effect based on prior general experience in rate of improver addition.

The improving effective amount of the composition may be selected to provide an equal amount of ascorbic

acid to that amount of ascorbic acid without the additional ingredients of the composition which would normally be employed in improving that particular type of dough. If this quantity is selected, an enhanced improving activity will be observed.

Compositions of the invention may include conventional adjuvants for baking additives of this type such as flow control additives and bulking agents, referred to herein collectively as bulking agents, to aid in convenience of measuring and handling. The invention also contemplates that other nonbromate improvers may be included in the normal proportions to ascorbic acid in which these other improvers are also employed. These other improvers may include azodicarbonamide, preferably encapsulated in accordance with our US patent application 07/738,968 filed August 1, 1991.

If the azodicarbonamide is encapsulated or is not present, fungal enzymes may also be incorporated in the compositions at concentrations capable of providing up to about 800 SKB per lb. of flour in the dough.

SKB units are a measure of alpha amylase activity in the fungal enzymes, the commercial available preparations of which normally contain other enzymes such as protease. The method of determining SKB units is given by

Association of American Cereal Chemists, 8th Edition, reprinted 1990, Official Method 22-01.

Ascorbic acid is normally employed in doughs at from about 10 to about 200 ppm. ADA may be employed in doughs from 0 to about 45 ppm.

Typical concentration ranges for use of AA, packaged in compositions of this type in particular types of dough, are:

TYPE OF BAKING	AA, P.P.M.
Sponge-Dough	10-100
Straight Dough	10-100
Water Brews	10-100
Flour Brews	10-100
No Time Dough	10-100
Continuous Mix	50-200
Frozen Doughs	50-200

It has been observed that the oxidized AA is stable in water solution for at best two to three hours so it is desirable to dissolve the compositions, if presolution is desired prior to direct addition to the dough, and then mix the solution with the dough promptly.

The following examples specifically illustrate the new concepts.

Example

Baking Comparison showing the Relative Improving Effect of Embodiments of the Invention Containing AA, Embodiments of the Invention Containing AA and ADA and AA by itself with and without ADA.

A standard bread dough was made up from the following ingredients:

	%
Flour	100
Salt	2
Dextrose	4
Yeast	3
Yeast Food (Bromate-Free) (see application S/N 07/738,968)	0.5
Shortening	2.5
Calcium Propionate	0.2
Emulsifier	0.1-0.5
Water	(amount needed for optimum absorption)

The ingredients are combined and mixed into a dough, such as straight dough, No Time and Frozen Doughs. The dough is mixed at ambient temperature except for Frozen Doughs, where dough is mixed at 20°C - 21°C and 4% lower water absorption. Doughs are allowed to rest for 10-15 minutes and placed into pans. The doughs are allowed to proof to constant height (2.5cm above pan), then baked

at 215°C - 216°C for 20 minutes.

Typical Product Formulations for Embodiments of the Invention

Ingredient	Formulation (ppm)		
	A	B	C
Ascorbic Acid	3.3	5.0	6.7
Ca peroxide	3.2	3.2	3.2
$FeSO_4$	0.7	1.0	1.0
Citric Acid	12.0	7.0	7.0
Sylox (SiO_2)	0.5	0.5	0.5
Wheat Starch (bulking agent)	80.3	83.3	86.3
pH of 0.5% Solution	3.6	3.8	4.0

Typical Addition rate 0.3g per 100g of flour

0.3g of each formulation adds: A 100 ppm AA

B 150 ppm AA

C 200 ppm AA

Comparison A

Comparison between no Improver Added to Dough, Unoxidized AA and AA Oxidized by the Invention

Doughs were mixed by the above described method for Frozen Doughs and all contained 800 SKB/lb of fungal alpha emylase.

Improver (ppm)	Specific Loaf Volume (cc/g)
Control (no improver)	5.4
AA (100)	5.9
Formulation A (AA = 100)	6.3

Comparison B

Comparison between no Improver Added to Dough, AA + ADA (encapsulated) and ADA Oxidized by the Invention + ADA (encapsulated)

The mixing and baking procedure and standard dough contents are similar to Comparison A.

Improver (ppm)	Specific Loaf Volume (cc/g)
Control (none)	5.4
AA (100) + ADA*(45)	6.1
Formulation A (AA = 100)+ ADA*(45)	6.8

*ADA encapsulated with fat according to US application 07/738,968.

As used herein the term "food approved acid" comprehends at least those acids, well known to those of skill in the art, as approved for use in food. Typical of these acids are acetic, citric, tartaric, propionic and the like as well as salts of various acids which on solution in water provide a pH in the preferred pH range such as $Ca(H_2PO_4)_2$ and the like.

Those acids and salts which are solid at ambient temperature are readily determinable by one of skill in the art.

"Food acceptable iron salts" include all sufficiently non-toxic iron salts well known to those of skill in the art and include ferric ammonium citrate, ferric phosphate, ferrous fumarate, ferrous gluconate, ferrous sulphate and ferric chloride. Hydrates of the iron salts are also contemplated.

"Food acceptable bulking agents" comprehends the usual inert agents used provide bulk or ease of handling to food additives for convenience in measuring and dispensing same. Silica, and starch are typical bulking agents.

CLAIMS:

1. A composition comprising calcium peroxide, ascorbic acid and an ingestible iron salt.

2. A composition according to claim 1 in which the iron salt is ferrous sulphate.

3. A composition according to claim 1 or claim 2, further comprising an ingestible bulking agent.

4. A composition according to any one of the preceding claims, further comprising azodicarbonamide.

5. A composition according to claim 4 in which the azodicarbonamide is encapsulated with an ingestible encapsulating agent.

6. A composition according to any one of the preceding claims, further comprising an ingestible acid.

7. A composition according to claim 6 in which the ingestible acid is solid at room temperature.

8. A composition according to claim 7 in which the ingestible acid is citric acid or $Ca(H_2PO_4)_2$.

9. A composition according to any one of the preceding claims which is a dry powder.

10. A composition according to any one of the preceding claims containing from 0.1 to 1 parts iron salt to 1 part ascorbic acid, by weight.

11. A composition according to any one of the preceding claims containing from 0.5 to 1.5 parts calcium peroxide to 1 part ascorbic acid, by weight.

12. A composition according to any one of the preceding claims, further comprising fungal enzyme.

13. A composition according to any one of the preceding claims, further comprising benzoyl peroxide.

14. An aqueous composition comprising a composition according to any one of claims 1 to 13 dispersed in water, and having a pH of 2.0 to 5.5.

15. A method of making dough in which calcium peroxide, ascorbic acid and an iron salt are dispersed in the dough.

16. A method according to claim 15 in which the dough is yeast-leavened.

17. A method according to claim 15 or claim 16 in which bromate oxidative improver is not used.

18. A method according to any one of claims 15 to 17 in which the calcium peroxide, ascorbic acid and iron salt are introduced to the dough as a composition according to any one of claims 1 to 14.

19. A method of making bread, in which dough for the bread is made in accordance with any one of claims 15 to 18.

20. A bread improver composition substantially as any described herein with reference to the examples, but not the comparative examples.

21. A method of making dough substantially as described herein with reference to the examples, but not the comparative examples.

22. A method of making bread substantially as described herein with reference to the examples, but not the comparative examples.

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Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

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Relevant Technical fields

(i) UK Cl (Edition L) A2B: BMB1; BMB9; BMB11; BMB19; BMB31; BMB39

(ii) Int Cl (Edition 5) A21D

Search Examiner: B J GARDNER

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI, US CLAIMS

Date of Search: 11 JANUARY 1993

Documents considered relevant following a search in respect of claims 1 TO 22

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1545320 (PENNWALT CORP) see particularly page 1 lines 85 to end and page 2 lines 1 to 52	1,14 and 15 at least
X	US 3954999 (VIDAL) see particularly column 1 lines 32 to 42 and 65 to end column 2 lines 1 to 25	1,14 and 15 at least

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

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